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# IMPROVED POLYOLEFIN-BASED SYNTHETIC FIBERS AND METHOD THEREFOR

## Field of the Invention:

5           The invention relates to a polyolefin-based synthetic yarn characterized by improved mechanical properties, improved dyeability and a method for making the yarn for use as carpet face yarn, textiles and upholstery.

## Background:

10           The invention is related to the invention described in application Ser. No. 08/787,241 to Mallonee, filed January 24, 1997, now U.S. Patent No. 5,811,040 which is a continuation-in-part of application Ser. No. 08/339,336 to Mallonee, filed November 14, 1994, now U.S. Patent No. 5,597,650 and a continuation-in-part of application Ser. No. 08/523,470 to Mallonee, filed  
15 September 5, 1995, now U.S. Patent No. 5,620,797.

          The invention is also related to application Ser. No. 08/407,507 to Mallonee, filed March 14, 1995, now U.S. Patent No. 5,587,118.

          Polyolefin-based yarns are characterized by a low cost and by a chemical resistance towards many liquids and are therefore of interest in for  
20 making carpet and textiles including upholstery yarn where staining is a problem. Polyolefin-based yarns are also suitable for technical applications, such as in filters. However, there are several disadvantages to conventional polyolefin-based yarns and fibers. For one, the glass transition temperature ( $T_g$ ) is below room temperature (i.e., between  $-5$  and  $-15^\circ\text{C}$ ). Due to the low  $T_g$  of polyolefin-based  
25 yarns, the shape retention of the yarn under an external force at room temperature is limited. Polyolefin-based yarns tend to adapt to a new shape through molecular motion in the polymer. As a result, the resilience of carpets made with a polyolefin-based yarn is undesirably low for use as a carpet fiber. At temperatures higher than room temperature, the resilience and other mechanical properties of

the yarn are even lower. Heat-setting the polyolefin-based yarn enables relaxation of the internal stresses in the yarn fibers and helps retain the shape for the yarn after twisting, but heat-setting can not lead to a permanent yarn shape if a sufficient external force is applied.

5           Another disadvantage of polyolefin-based yarns is that the yarns are only slightly dyeable with dispersed dyes and are not dyeable at all with reactive dyes. The dye fastness of such yarns is often unsatisfactory even when washing the yarns at low temperatures.

10           Of the other synthetic fibers, nylon has been the main choice for carpets, where high quality and resilience is required. However, nylon is not without drawbacks. Notably, carpeting made with nylon yarn is susceptible to developing static electrical charges and thus must be chemically or physically treated to reduce the building up of static charges. Another disadvantages of nylon carpeting is that it will readily stain. Accordingly, nylon carpeting usually  
15 contains treatments which reduce its staining tendencies. These treatments do not, however, prevent all staining, nor will the treatments be effective for the life of the carpet.

          On the other hands, carpets made from polyolefin materials, such as polypropylene, are very resistant to staining and are naturally antistatic. However,  
20 as set forth above, polypropylene is a less resistant fiber and will not maintain its appearance or shape under prolonged or heavy use or after repeated deformations.

          Similar considerations with respect to polyolefin-based yarns can be addressed for the textile sector, including upholstery yarns, where stain removal is extremely difficult. The use of the polyolefin-based yarns could be even more  
25 beneficial due to the low costs of the polymer and to its excellent hydro-repellency, dry fastness and resistance to staining. Unfortunately, use of polyolefin-based yarns is limited by its low mechanical properties and limited shape retention due to the low resilience of such yarns and to the fact that

mechanical properties of such yarns at temperatures above room temperature tend to decrease rapidly.

Standard dyeing techniques using a dye bath are not possible with polyolefin-based yarns as is the case for the polyester or for nylon fibers. Accordingly, polyolefin polymers or copolymers, such as ethylene/acrylic copolymers, have been used in conjunction with the polyolefin-based yarns. Other additives with similar properties were developed to introduce amino groups in the polyolefin polymer during the polymerization phase. To obtain dyeability of polyolefin-based yarns with disperse dyes, polyester-based additives and polar copolymers were used. Dyeing of polyolefin-based yarns with ligand-forming dyes was made possible through the addition of nickel compounding. Dyeing with hydrocarbon soluble dyes with long alkyl-chains was also proposed for standard polyolefin polymers. A dyeable polypropylene polymer was provided by the use of special dendrimers and hyperbranched polymers. Plasma treatments have been proposed on a laboratory scale to introduce reactive groups into the yarn surface.

While the foregoing developments have had limited success, all of the foregoing techniques suffer from an increase in cost, which reduces the competitiveness of the polymer, the mechanical properties of the resulting yarn, the spinnability of the yarns and may adversely affect the thermal stability of the yarn. The stain resistant properties of such yarns and the color fastness of dyed fibers are also unacceptable or are reduced below desired values.

There continues to be a need for improved polyolefin-based yarns and fibers for use in carpets, textile, upholstery and other applications where the properties of polyolefin materials may be beneficial.

#### **Summary of the Invention:**

With regard to the above and other objects, the invention provides a method for making fibers and yarns having denier per filament (dpf) size ranging

from about 1 to about 30 dpf and improved mechanical properties. The method includes blending from about 55 to about 95 wt.% polyolefin polymer and from about 5 to about 45 wt.% fibril forming polymer to provide a mixture of polyolefin and fibril forming polymers. A hot melt extruder to which the mixture is fed is  
5 used to provide a substantially homogenous molten mixture of polyolefin and fibril forming polymers. The molten mixture is then forced through a spinneret having an length to diameter (L/D) ratio ranging from about 3 to about 30 at a shear rate ranging from about 1000 to about 5000 reciprocal seconds to provide a fiber having a polyolefin matrix and elongate, substantially discontinuous fibrils of  
10 the fibril forming polymer dispersed in the polyolefin matrix, whereby an exterior surface of the fibers is substantially devoid of fibrils.

In another aspect the invention provides a yarn having improved mechanical properties and enhanced dyeability. The yarn includes from about 55 to about 95 wt.% polyolefin continuous phase and from about 5 to about 45 wt.%  
15 discontinuous phase of fibrils dispersed in the polyolefin continuous phase, the fibrils being derived from a fibril forming polymer selected from the group consisting of polyamide polymers and polyester polymers. The polyolefin continuous phase is substantially devoid of fibrils on an exposed surface thereof, the yarn is dyeable with reactive dyes such as acid or cationic dyes, and the yarn  
20 exhibits an irreversible deformation at about 25°C of less than about 3 %.

The present invention is an improvement on the invention described in related U.S. Patent Nos. 5,587,118; 5,597,650; 5,620,797; and 5,811,040 to Mallonee, which provides a method for blending immiscible polymers to provide an improved carpet face yarn. It has been found that filaments made according to  
25 the invention have a substantially continuous polyolefin phase and a substantially discontinuous fibril phase interspersed in the polyolefin phase. The discontinuous fibril phase provides to a polyolefin-based carpet yarn, polyamide- and/or polyester-type properties in terms of resiliency and color fastness, but without the

apparent characteristic drawbacks of the material forming the fibrils. That is, the yarn exhibits the excellent anti-staining properties of polyolefin and their favorable flame retardancy and anti-static properties, but does not exhibit the weak points of the conventional polyolefin fibers. The yarn is also less costly to produce than many polyamide and polyester filaments, since polypropylene is currently up to about 60% cheaper per pound than polyamide and up to about 40% cheaper than polyester.

In addition to the foregoing properties, the yarn of the invention comprising polyolefin matrix and polyester fibrils has a matt finish thus reducing the need for the addition of fillers such as titanium dioxide to decrease the luster of the yarn as is required with conventional polyamide carpet yarns.

#### **Brief Description of the Drawings:**

Further advantages of the invention are apparent by reference to the detailed description when considered in conjunction with the figures, wherein like reference numbers indicate like elements throughout the several views, and wherein:

Fig. 1 is an illustration, not to scale, of a preferred spinneret orifice configuration for producing synthetic fibers according to the invention;

Figs. 2 and 3 are cross-sectional illustrations, not to scale, of trilobal or delta-shaped synthetic fibers made according to the invention;

Fig. 4 is a graphical comparison of tenacity values for fibers made from single polymers and blends of polymers;

Fig. 5 is a photomicrograph of a polyolefin fiber after chemical etching made by a process wherein an L/D ratio of a spinneret used to make the fiber is less than 3;

Fig. 6 is a photomicrograph of a polyolefin fiber after chemical etching made by a process according to the invention wherein an L/D ratio of a spinneret used to make the fiber is 3;

5 Fig. 7 is a photomicrograph of a polyolefin fiber after chemical etching made by a process according to the invention wherein an L/D ratio of a spinneret used to make the fiber is 6;

Fig. 8 is a photomicrograph of a polyolefin fiber after chemical etching made by a process according to the invention wherein an L/D ratio of a spinneret used to make the fiber is 15;

10 Fig. 9a is a digital image of a woven cloth sample made with a conventional polyester yarn after 2500 brush cycles;

Fig. 9b is a digital image of a woven cloth sample made with a fiber according to the invention after 10,000 cycles; and

15 Fig. 10 is a graphical comparison of mechanical properties of fibers made according to the invention (plots A and B) and of pure polyolefin fibers (plots C and D) with thermal treatment (plots B and D) and without thermal treatment (plots A and C).

#### **Detailed Description of the Preferred Embodiments:**

20 The synthetic fibers and yarns made according to the invention using a blend of immiscible polymers preferably have a denier per filament (dpf) size ranging from about 1 to about 30. Because the polyolefin and fibril-forming polymer immiscible with the polyolefin are melt blended and forced through capillary openings of a spinneret as a molten blend, each of the resulting filaments  
25 contains essentially the same amount of polyolefin and fibril-forming polymer as the molten blend.

The resulting fibers are characterized by a polyolefin continuous phase matrix having interspersed therein substantially co-linear, discontinuous,

elongate fibrils throughout the matrix. An important feature of the synthetic, polyolefin-based yarn of the invention is that it has a resiliency similar to polyamide yarns such as nylon 6 and nylon 66, yet has the stain resistance of polyolefin yarns such as polypropylene. Furthermore, the synthetic yarn of the invention has a much higher dyeability, flame retardance and mechanical resistance at temperatures higher than room temperature than pure or virgin polyolefin polymer. Finally, the synthetic yarn of the invention is resistant to the formation of a static electric charge common to polyamide-based carpet yarns.

In order to provide a suitable blend of immiscible polymers for making the synthetic fibers and yarns, a mixture containing from about 55 % to about 95% by weight polyolefin is blended with from about 5 to about 45% by weight fibril forming polymer. It is preferred that the blend of polyolefin and fibril-forming polymer used to make the fibers and yarns of the invention contain from about 60 to about 95 wt. %, more preferably from about 70 to about 85 wt. %, and most preferably 75 wt.% polyolefin. The fibril forming polymer is preferably present in the blend in an amount ranging from about 5 to about 40 wt. %, more preferably from about 15 to about 30 wt. %, and most preferably 25 wt% fibril- forming polymer.

The polyolefins which may be used to produce the yarn and fibers of the invention include, but are not limited to, polyethylene, polypropylene, both homopolymer and copolymers, poly(1-butene), poly(3-methyl-1-butene), poly(4-methyl-1-pentene) and the like as well as combinations or mixtures of two or more of the foregoing. Of the polyolefin polymers mentioned above, polypropylene homopolymer is particularly preferred. Bulk polypropylene suitable for making the yarn of the invention is available from, but not limited to, Shell Chemical Company of Houston, Texas, under the trade name designations NRDS-126-3, 5E40 and 5E70, Basell Polyolefins Company N.V. of Brussels, Belgium under the trade names MOPLEN X69S, ADSTIF 855 ADXP, X50251, ADFLEX X102S



and Aristech Chemical Company of Pittsburgh, PA, under the trade name D-115-F and D-080-A.

5 The fibril-forming polymer blended with the polyolefin to make the filaments may be selected from the group consisting of polyamide and / or polyester. Polyamide polymers which may be used include the condensation product of a dibasic acid and a diamine such as adipic acid and hexamethylene diamine (nylon 66), and the addition reaction products of monomers containing both an acid and an amine group in the molecule, such as the polymerization product of e-caprolactam to form polycaproamide (nylon 6). Higher analogs or  
10 blends of nylon 6 and 66 may also be used. Of the foregoing, nylon 6 is the most preferred polyamide for use in forming the carpet face yarn of the invention. Suitable sources of polyamide polymers include, but are not limited to, the nylon 6 polymers available from AQUAFIL S.P.A. of Arco, Italy, under the trade name AQ2700 and from BASF Corporation of Asheville, N.C. under the trade name  
15 designation Type 403. Other sources of polyamide polymer may be suitable as well.

Polyester polymers which may be used to make the yarn of the invention include, but are not limited to, the polycondensation products of dicarboxylic acids or anhydrides with dihydric alcohols and mixtures of the  
20 polycondensation products. Dicarboxylic acids and anhydrides which may be reacted with the dihydric alcohols include the saturated or unsaturated fatty acids and anhydrides such as maleic, fumaric, phthalic and adipic acids and anhydrides. A particularly preferred dicarboxylic acid or anhydride is phthalic acid or anhydride.

25 The dihydric alcohols which are reacted with the dicarboxylic acids or anhydrides to provide the polyester polymers include, but are not limited to, the alkylene glycols having from about 2 to about 10 carbon atoms. Preferred dihydric alcohols include ethylene glycol, propylene glycols, diethylene glycol and

dipropylene glycol. Particularly preferred polycondensation products of dicarboxylic acids or anhydrides and dihydric alcohols include polyethylene terephthalate, polybutylene terephthalate and polytrimethylene terephthalate.

5 A suitable source of polyester polymer is the polyethylene terephthalate polymer available from Wellman Corporation, of Johnsonville, S.C. under the trade name designation PERMACLEAR PET. Other sources of polyester polymer which may be used include polybutylene terephthalate polymer available from Montefibre of Milano, Italy under the trade name TQ9/04/N and from BASF Corporation of Portsmouth, Virginia under the trade name  
10 ULTRADUR B 4500. Another source is polytrimethylene terephthalate available from Du Pont Company of Wilmington, Delaware under the trade name 3GT or SONORA and that of Shell Chemical Company under the trade name CORTERRA as well as other suitable sources.

In addition to the polyolefin and fibril forming polymers, the blend  
15 may contain from about 0 wt. % to 20 wt. % interphase modifier. Interphase modifiers that may be used, can be selected for several polyolefin polymers reacted with acids or anhydrides including fumaric acid, acrylic acid or methacrylic acid as well as maleated polyolefins. Examples of maleated polyolefins include maleated ethylene-propylene, maleated styrene-butadiene-  
20 styrene, maleated styrene-ethylene-butadiene-styrene, maleated ethylene-propylene rubber (EPR), maleated ethylene-propylene-diene monomer (EPDM) and mixtures thereof. Sources of maleated polyolefins include, but are not limited to, POLYBOND 3200 available from Uniroyal Chemicals of Middleburg, Connecticut and EPOLENE E-43 available from Eastman Chemical Company of  
25 Kingsport, Tennessee.

The synthetic yarn of the invention may also contain any one or more additives selected from flame retardants, dyes, pigments, antioxidants, fillers, antistatic agents, melt processing aids, UV and thermal stabilizers, plasticizers and

the like. A particular advantage of the invention is the synergistic flame retardance of the yarn and fibers. Even though the filaments of the yarn may contain a non-halogenated fibril-forming polymer and no flame retardants, the yarns according to the invention may exhibit about 45 to about 75% increase in flame retardance relative to the flame retardance of pure polyolefin yarn. In order to further improve the flame retardance to the synthetic yarn of the invention, the fibril forming polymer may be halogenated. For example, one or both of the dicarboxylic acid or anhydride and dihydric alcohols used to make the polyester polymer, may be halogenated. Halogens which may be used include chlorine, bromine, and fluorine. Halogenated polyester compounds prepared from the halogenated acids or alcohols may also be mixed with other well known halogenated and non-halogenated flame retardants if desired to further increase the flame retardancy of the fibers and yarns of the invention.

When desired, the polyolefin/fibril forming polymer mixture of the invention may also contain other flame retardants. Flame retardants suitable for use with one or both the components of the mixture include, but are not limited to, brominated polystyrene, hexabromocyclododecane, decabromodiphenyl oxide, ethylene-bis(tetrabromophthalimide), ethylene-bis(dibromonorborane dicarboximide), pentabromodiphenyl oxide, octabromodiphenyl oxide, decabromodiphenoxyethane, poly-dibromophenylene oxide, halogenated phosphate ester, tetrabromophthalic anhydride, bis(tribromophthalic anhydride), tetrabromobisphenol-A bis(2-hydroxyethyl-ether), tetrabromobisphenol-A bis(2,3-dibromopropyl ether), dibromo-neopentyl glycol, tetradecabromodiphenoxy benzene, aluminum oxide trihydrated, antimony oxide, sodium antimonate, zinc borate, di-acrylate ester of tetrabromobisphenol-A and the like and mixtures thereof.

A preferred flame retardant system will generally contain a halogenated organic compound and a flame retardant synergist such as antimony

oxide. The total amount of flame retardant in the yarn may range from about 5 to about 15 wt. % of the total weight of fibers. At about 10 wt. % flame retardant, there is often about a 50% increase in flame retardance as determined by the radiant panel flame retardance test.

5 Thermal stabilizers useful with the components used to produce the fibers of the invention include, but are not limited to, calcium powders, calcium stearate, phenols and hindered phenols, zinc oxide, aryl esters, hydroxybenzophenone, hydroxybenzotriazole and the like.

10 Antioxidant additives may be selected from alkylated phenols and bisphenols, alkylidene-bisphenols, alkylidene-trisphenols, alkylidene polyphenols, thiophenols, dithio-bisphenols, dithio-trisphenols, thio-polyalkylated phenols, phenol condensation products, amines, dilauryl thiodipropionate, distearyl thiodipropionate, dimyristyl thiodipropionate, ditridecyl thiodipropionate, pentaerythritol tetrakis(b-lauryl thiopropionate), p-benzoquinone, 2,5-ditert-butylhydroquinone and the like.

15 Antibacterial and anti dust-mites additives may also be used. Among these, the inorganic, glassy phase or zeolite-based additives may be selected. Other types of antibacterial, anti dust-mites additives may also be used.

20 The polyolefin, fibril-forming polymer and optional additives may be combined in a variety of ways, however it is preferred to dry blend the components prior to feeding the blend to an extruder. In the alternative, each of the polyolefin, fibril-forming polymer components and optional ingredients may be fed directly to the extruder in any order provided there is sufficient residence time in the extruder to assure substantially homogeneous mixing of the components. It will be recognized that a preblended essentially homogeneous mixture of polyolefin and fibril-forming polymer may also be fed to an extruder.

25 With respect to a polyester fibril-forming polymer, once combined, the mixture of polyolefin and polyester is melt-blended and extruded under

pressure to provide an essentially homogenous mixture of the two components. Pressures ranging from about 700 to about 2000 psia (about 4.8 MPa to about 13.8 MPa) are preferably used to obtain a homogeneous mixture of the components prior to extrusion. The molten mixture is forced from the extruder spinneret at a temperature within the range of 240° to about 300°C through the spinneret openings. The extruder temperature used is a function of the viscosity of the fibril-forming polymer in the blend. Where the fibril-forming polymer has a higher viscosity, higher extrusion temperatures should be used. For example, when using nylon 6 the extrusion temperature is preferably in the range of from about 250° to about 290°C. When using polyethylene terephthalate the extrusion temperature is preferably in the range of from about 260° to about 300°C.

The following figures may be used to illustrate other aspects of the invention. FIG. 1 illustrates a capillary opening (10) for a spinneret for use in producing filaments for making fibers and yarns according to the invention. The capillary opening is preferably a trilobal capillary configuration. The capillary opening (10) has legs (12) of substantially equal length so that the melted mixture flows through the capillary opening (10) in legs (12) thereby increasing the shear rate on the molten mixture and causing the filament to set in a generally trilobal cross-sectional configuration (14) as illustrated in FIG. 2 or a delta cross-sectional configuration (16) as illustrated in FIG. 3. In FIGS. 2 and 3, the polyolefin (18) provides the bulk of the filament with elongate, longitudinally oriented fibrils (20) made of the fibril forming polymer dispersed within the filament generally concentrated toward the center of the filament.

The shear rate of the molten mixture during extrusion is another important factor in practicing the present invention for optimal results. Shear rates in the range of from about 1000 to about 5000 reciprocal seconds are preferred. Particularly preferred is a shear rate within the range of from about 2000 to about 4000 reciprocal seconds, with a shear rate of from about 2500 to about 3800

reciprocal seconds being especially preferred. By selecting a plurality of capillary openings of an appropriate size having a trilobal arrangement, the desired shear rate for extrusion of the mixture may be obtained.

5 A particularly important parameter to be taken into consideration is the ratio of depth or length (L) of the capillary hole to the average hydraulic diameter (D) of the capillary 10 through which the molten mixture is forced. A preferred L/D ratio is in the range of from about 3 to about 30, depending on the melt viscosity of the polyolefin and of the fibril forming polymer and on the shear rate in the capillary opening 10. A ratio in the range of from about 6 to about 10 is  
10 preferably used to minimize or substantially eliminate fibrils on an exterior surface of the filaments. Reactive dyeability of the fibers using acid or cationic dyes, may be enhanced by use of an L/D ratio ranging from about 1 to about 3. Accordingly, an appropriately selected L/D ratio enhances the concentration of the fiber forming polymer inside the polyolefin matrix and reduces the average diameter of the  
15 fibrils.

While not desiring to be bound by theoretical considerations, it is believed that the properties of the fibers and yarns of the invention are due, at least in part, to the in-situ formation of elongated, substantially discontinuous fibrils in a continuous polyolefin phase. The in-situ fibril formation is believed to be  
20 promoted by the immiscibility of the components of the mixture with one another, and the shear forces exerted on the molten mixture as it is forced through the capillary openings 10 of the spinneret. The presence of a compatibilizer aids to increase the spinnability and the mechanical strength of the interface between the polyolefin matrix and the immiscible polymer.

25 During extrusion, the forming polymer fibrils concentrate in generally longitudinally aligned orientation toward the center of the capillary openings 10 of the spinneret where the shear forces are the least. As a result, the elongate fibrils are interspersed in a continuous polyolefin phase which is

concentrated near the walls of the capillary openings of the spinneret where the shear forces are the greatest. Polyamide and/or polyester fibrils and/or other polymers fibrils immiscible with polyolefin which are produced by the shear forces associated with passage of the material through the capillary openings 10 have a diameter in the range of a fraction of a micron to a few microns and a length of several tens of microns, whereas the overall cross-sectional length of each side of the trilobal or delta filaments containing the fibrils may range from about 1 to about 3 millimeters. Typically, the fibrils will have an average diameter of from about 0.1 to about 5 microns and an average length ranging from 10 about 100 to about 1000 microns, depending on viscosity ratio and spinning parameters.

Through a phenomenon not fully understood, the polyolefin forms into a continuous phase providing a matrix encapsulating the polymeric fibrils. The polymeric fibrils provide reinforcing to the polyolefin matrix similar to 15 reinforcing provided by fiberglass in a thermoplastic or thermoset resin. Accordingly, the polymeric fibrils which are more resilient than the polyolefin improve the resiliency of the yarn and fibers over conventional polyolefin fibers and yarns making an excellent material for carpet face yarn, textiles and upholstery.

20 Another factor which is believed to contribute to the formation of fibrils in the center of the filament is the difference in the melt viscosity between the polyolefin and fibril-forming polymer phases. The generally lower polyolefin melt viscosity may cause the polyolefin to flow much more readily through the capillary opening 10 at the walls of the opening where the shear rate is highest, 25 while the more viscous fibril-forming polymer concentrates into areas of the capillary opening 10 away from the walls. For example, at a shear rate of 3800 reciprocal seconds, polypropylene has a melt viscosity of about 240 poises at 280°C, at the capillary wall. The melt viscosity for the same temperature and

shear rate for polyester having an intrinsic viscosity of 0.64 is 2600 poises and is 7800 poises for polyester having an intrinsic viscosity of 0.81 at 280°C. Accordingly, the ratio of polyester polymer melt viscosity to polyolefin melt viscosity is preferably within the range of from about 10:1 to about 40:1 for producing the filaments of the invention containing polyester fibrils in a polyolefin matrix.

At a shear rate of 2500 reciprocal seconds, polypropylene has a melt viscosity of 330 poises at 260°C, at the capillary wall. The melt viscosity for the same temperature and shear rate for nylon 6 having a relative viscosity of 2.4 is 700 poises and is 1160 poises for nylon 6 having a relative viscosity of 2.7. Accordingly, the ratio of polyamide polymer melt viscosity to polyolefin melt viscosity is preferably within the range of from about 2:1 to about 3:1 for producing filaments containing polyamide fibrils in a polyolefin matrix.

After spinning, the filaments are drawn one or more times, preferably three times, and then texturized with either a hot air jet or a steam jet. Spinning, drawing and texturizing can be done both with the one-step or with the two step process, depending on the type of final product desired, like BCF yarn, CF yarn, POY yarn, FDY yarn, staple fibers and with parameters set as a function of the specific facilities employed. The filaments of the invention may be spun, drawn and texturized essentially continuously without the need for an intermediate curing or a waiting period. In the alternative, an intermediate waiting period may be used between the spinning, drawing and/or texturizing steps.

For purposes of obtaining colored carpet face yarns, the components which are combined to make the yarns of the invention may each contain pigments or chemical dyes, or the finished yarn or fibers may be dyed. Useful inorganic pigments include, but are not limited to, cadmium mercury, cadmium mercury orange, cadmium sulfide yellow, cadmium sulfoselenide, titanium dioxide, titanium yellow, titanium green, titanium blue, cobalt aluminate, manganese blue,



manganese violet, ultramarine red, ultramarine blue, ultra- marine violet, and the like. Organic pigments include, but are not limited to, permanent red 2B, perylene red, quinacridone red, diazo orange, otiazo yellow, isoindolinone, hansa yellow, phthalocyanine green, phthalocyanine blue, quinacridone violet, dopamine violet and the like.

Chemical dyes include, but are not limited to, the mono- and disulfonated acid dyes, as well as triphenylmethane, pyrazolone, azine, nitro and quinoline dyes. When used, the pigment dyes may be predispersed in the polyolefin master batch before the polyolefin and fibril-forming polymer are extruded, or may be introduced after the extrusion process using a side extruder system.

Since pure polyolefin filaments cannot generally be dyed with chemical acid or cationic dyes, pigment dyes are typically used during yarn manufacturing to give the polyolefin its color in a process known as "solution dyeing". Solution dyeing results in a permanent color that is highly resistant to staining or fading due to UV light.

In contrast to conventional polyolefin fibers and yarns, the fibers and yarns of the invention may be dyed with disperse dyes, in addition to the use of pigment dyes during manufacturing, and once dyed, the fibers and yarns of the invention have been found to exhibit stain resistant properties similar to pure polyolefin fibers and yarns.

Moreover, when the fibril-forming polymer used with the polyolefin to make the filaments is a polyamide, it is also possible to dye the yarn of the invention using acid or cationic dyes. However it is preferred to use a mixture of an acid dye and a disperse dye to dye the filaments. The mixture of dyes may contain from 0 to about 50 percent disperse dye and from about 50 to about 100 percent acid dye. A particularly preferred dye is a mixture of about 50 percent by weight acid dye and about 50 percent by weight disperse dye.

When the polymer used is polyester, a disperse dye is preferably used. Disperse dyes are generally used with a carrier fluid which is compatible with the particular dye. Suitable carrier fluids are known to those of ordinary skill in the art. The amount of dye in the carrier fluid used to color the filaments may  
5 range from about 0.15 to about 0.7 percent by weight of the dye and carrier fluid, preferably from about 0.2 to about 0.5 percent by weight of the dye and carrier fluid.

In order to dye the filaments, the filaments are preferably first washed with hot water usually containing about 0.5 % by weight of a base such as  
10 NaOH, KOH or  $\text{NH}_3\text{OH}$ . The temperature of the hot water wash ranges from about 60° to about 80°C, and should be hot enough to remove any residual finish oils which may be on the filaments.

After washing, the filaments are preferably dyed in a dye bath at about 90° to about 100°C, for at least 15 minutes or longer. A fiber or yarn made  
15 of a polyolefin/polyester mixture may be dyed using from about 0.2 to about 0.6 percent by weight disperse dye at the same temperature and pressure or at a temperature ranging from about 115°C to about 120°C, while maintaining the dye under a slight pressure.

When a fibril forming polyamide base polymer is used, or any other  
20 polymer containing reactive groups, like the amine group  $-\text{NH}_2$  or the  $-\text{COOH}$  group, the polyolefin based synthetic yarn of the invention may be dyed with acid or cationic reactive dyes, with or without disperse dyes, using high pressure systems with pressures ranging from about 1 to about 5 bars. In this case a very high stable color fastness towards washing, shampoo, UV light, ozone may be  
25 obtained for fibers and yarns exposed to temperatures up to about 100°C.

Various features and aspects of the invention will now be illustrated with reference to the following non-limiting examples.

### Example 1

Two types of polypropylene polymer were evaluated in a dry blend mixture containing 15 wt.% nylon 6 pellets having a relative viscosity of 2.7 (type BS-700 from BASF Corporation) and 85 wt.% polypropylene pellets having a melt index of 20 (5-1466 from Union Carbide Corporation) and polypropylene pellets having a melt index of 9 (5E40 from Union Carbide Corporation). The 5E40 pellets had a crystallinity ratio of 50 to 55%. The dry blend mixture was fed from a feed hopper directly into a 1 ½ inch hot melt extruder wherein a homogeneous molten mixture was obtained. The 85 wt.% polypropylene portion consisted of 4 wt.% beige color concentrate (SCC-13524 from Standridge Color Corporation) and 2 wt.% grafted maleic anhydride (POLYBOND 3200 from Uniroyal Chemical Company). The molten mixture was then pumped through a pack of screens to remove any particles greater than 20 microns. The screened mixture was pumped to a spinneret having 67 trilobal capillary openings in order to form filaments. Each trilobal capillary had leg lengths of 0.0205 inch and leg widths of 0.008 inch. The extrusion rate was 0.25 pounds per hour per capillary opening at 260°C thereby producing a shear rate of 3245 reciprocal seconds. Carpet yarn was spun from the filaments thus formed in a one-step process. The spin-draw was done using nylon 6 extrusion conditions at 1200 m/min. The trilobal-shaped filaments were spun at a denier of 3900 per 67 filaments at a temperature of 256°C. The yarns were drawn three times at 125°C and hot air jet texturized at 150°C. Drawing yielded a textured yarn having a denier of 1150 per 67 filaments. The relaxation ratio was 0.71:1 and the drawn denier was targeted for 1150 with 67 filaments. The physical properties of yarns made according to this process and comparative yarns are given in the following Table 1.

Table 1

Run No.	Description	Denier	Tenacity		Elongation at break (%)	Bulk (%) (125°C)
			g/den.	g/dtex		
1	PP Control (5E40)	1152	2.7	2.40	122	21
2	PP Control (5-1466)	1148	2.5	2.25	115	17

3	85wt.% PP (5-1466) 15wt.% PA (BS-700)	1147	2.5	2.25	64	16
4	85wt.% PP (5E40) 15wt.% PA (BS-700)	1145	2.8	2.50	74	18
5	PA Control (BS-700)	1149	3.2	2.90	88	17

As shown by the foregoing examples, mixtures of polypropylene and nylon exhibited substantially lower elongation than the pure polymers of either polypropylene or nylon while the other properties of the fibers were substantially the same. The fiber made with nylon 6 and polypropylene having a melt index of 9 exhibited the highest tenacity and elongation at break of the mixed polymers.

#### Example 2

Carpet face yarns were made from the fibers formed in Example 1.

In order to form a suitable carpet face yarn, the 1150 denier polyolefin/nylon (PP/PA) filaments were twisted and heat set. Twisting of the filaments was at 4.25 X 4.25 tpi and the yarn was heat set on a SUPERBA stuffer box at a tunnel temperature of 132°C for the polypropylene control sample and 121°C for the nylon control sample.

Once twisted and heat set, the yarn of the invention was broadloom tufted in 28 ounce cut pile having 24 stitches and 21/32 inch pile height. Floor ratings of the yarns are given in the following Table 2. Floor ratings were made after 20,000 traffics.

Table 2

Run No.	Description	Floor Rating
1	PP Control (5E40)	2.00
2	PP Control (5-1466)	1.75
3	85wt.% PP (5-1466) 15wt.% PA (BS-700)	2.25

4	85wt.% PP (5E40) 15wt.% PA (BS-700)	3.25
5	PA Control (BS-700)	2.75

As shown by the foregoing comparisons, carpet formed from the PP/PA fibers exhibited a Carpet Research Institute (CRI) floor rating 29-62% better than pure polypropylene yarn and Run 4 exhibited a floor rating of 18 % better than pure nylon yarn.

### Example 3

Spinning tests using several polypropylene (PP) types, namely UC 1465 and UC 5E40 from Union Carbide and XA16 from Amoco, were performed. The selected polypropylene and the nylon 6 with a relative viscosity of 2.7 (AQ 27000 from Aquafil), were separately fed from two hoppers into the extruder of the spinning plant for the production of carpet face BCF yarn. A polypropylene based compatibilizer, containing maleic anhydride pre-grafted with a polypropylene molecule (PP-AM) was introduced by means of a third hopper into the extrusion system. A standard Barmag metering screw was used during trials.

A spinneret with 64 holes, having an L/D ratio of 3 was used, with a shear rate at the capillary of about 2900 reciprocal seconds. Blends of the polymers are given in Table 3. Before feeding the extruder, both the nylon 6 (PA6) and the PP-AM were dried. The moisture content in the PA6 was 300 ppm.

Extrusion was performed in a 2 ½ inch metering screw. The molten mixture was pumped into a pack of screens to remove any particles greater than 30 micron. The screened blend was pumped into a spinneret with 64 trilobal holes. The yarn was then drawn with a drawing ratio of 4 and texturized with hot air at 130°C. Processing was performed at a drawing speed of 2200 m/min. The final yarn count was 1330 dtex. Properties of the yarns are given in the following Table 3 and the tenacity of the yarns are illustrated in Fig. 4.

**Table 3**

Type of Polymer	PP (wt.%)	PA6 (wt.%)	PP-AM (wt.%)	Tenacity (g/dtex)	Elongation at break (%)	Bulk (air 130°C)
AQ 2700	0	100	0	2.63	66	---
PP A (UC 1465)	100.0	0	0	1.55	115	12.1
PP A (UC 1465)	82.3	15	2.8	1.80	65	8.9
PP B (UC 5E40)	100.0	0	0	2.15	66	---
PP B (UC 5E40)	83.0	15	2	2.35	55	
PP B (UC 5E40)	84.0	15	1.0	2.36	47	---
PP C (XA16)	100.0	0	0	2.20	96	13.1
PP C (XA16)	83.0	15	2	2.45	60	9.3

A comparative test on the same spinneret was performed using a pure PA 6 polymer. Results indicate that independently from the polypropylene chosen, higher tenacity values were achieved by manufacturing the yarn according to the invention, as evidenced by Fig. 4. Moreover a yarn with a higher dimensional stability after heat treatment at 130°C in air was produced.

**Example 4**

Blended yarns were made using polypropylene (PP) (UC 5E40 from Union Carbide) and nylon 6 (PA) (AQ 27000 from Aquafil) using variable amounts of PA and PP and different yarn counts. The results are shown in the following Table 4.

Table 4

Run No.	Yarn Count (den.tex)	PP (wt.%)	PA6 (wt.%)	PP-AM (wt.%)	Tenacity (g/dtex)	Elongation at break (%)	Bulk (air 130°C)
1	1330	100	0	0	2.20	96	13.1
2	1330	83	15	2	2.45	60	9.3
3	1330	100	0	0	2.20	96	13.1
4	1330	83	15	2	2.45	60	9.3
5	1020	85	15	2	2.35	74	10.1
6	1729	83	15	2	2.35	57	10.2
7	1330	78	20	2	2.35	58	9.6
8	1330	73	25	2	2.30	56	9.5
9	1330	63	35	2	2.20	61	9.2

The foregoing results demonstrated that physical properties of the yarns made according to the invention did not vary significantly with the concentration of components. The blends shown in Table 4 demonstrated the applicability of the yarn made according to the invention over a wide range of compositions.

Example 5

In order to evaluate the performance of the synthetic yarn as a face carpet yarn, a 1330/64 x 2 air-entangled yarn was manufactured. The yarn was tufted on a 1/10 inch tufting machine, with a pile height of 5 mm and two different constructions, in order to reach a pile density of 450 and 550 g/m<sup>2</sup>. The carpet was dyed in bath using disperse dyes (Dystar dispersed dyes) and tested under the castor chair and Vetterman Drum test. The Vetterman Drum test simulated wear according to ASTM D5417. The degree of wear exhibit by the samples was determined by a visual rating relative to photographic standards of wear from The Carpet and Rug Institute (CRI Reference Scale available from CRI, P.O. Box 2048, Dalton, Ga., USA). Each of the common types of carpet construction has a corresponding set of photographic examples of unworn and worn samples. The wear levels range from 5 to 1, where 5 represents no visible wear and 1 represents considerable wear.

The results of a castor chair test and Vetterman Drum test were determined on 450 and 550 g/m<sup>2</sup> carpets made with yarn made according to the invention compared with the carpet made using 100 wt.% nylon 6 ( PA) and 100 wt.% PP yarns having the same characteristics. Results are presented in Table 5 as a function of carpet density and of polymer type.

Table 5

Polymer		100 wt.% PA		100 wt.% PP		85 wt. % PP 15 wt.% PA	
Carpet pile density	(g/m <sup>2</sup> )	450	550	450	550	450	550
Vetterman 5000	Wear level	2.5	3	2	2	2.5	2.5
Vetterman 22000	Wear level	2.5	2.5	1.5	2	2	2
Castor Chair final	Wear level	1.88	1.88	1.88	1.88	1.88	1.88

As shown by the foregoing comparisons, yarn made according to the invention exhibited a wear behavior which is better than that of the pure PP yarn and comparable to that of the pure nylon 6 carpet.

Example 6

Spinning of a blend containing 20 wt.% nylon 6 and 3 wt.% of compatibilizer was performed using different spinnerets characterized by L/D ratios ranging from 2 to 15. The spinnerets were manufactured with different sizes, in order to maintain a constant shear rate of about 2900 reciprocal seconds. Spinning characteristics of the 1330 dtex / 64 filament BCF yarn was similar to that of Example 3.

After spinning a metallographic analysis was performed to evaluate the distribution of the nylon 6 in the filaments. The surface of the filaments was analyzed using a Jeol Scanning Electron Microscope (SEM) at the laboratories of the University of Trento in Italy before and after their immersion in acetic acid in



order to remove nylon 6 on the external surface of the yarn. The photomicrographs labeled Figs. 5-8 show the amount of nylon 6 present on the external surface of the filaments available for staining or soiling as dark space or holes where the nylon 6 was dissolved by the acid from the surface of the filaments for each of the L/D ratios used.

Results of the analysis done on the BCF yarn produced respectively using a L/D ratios of 2, 3, 6, 15 showed that a substantial amount of nylon 6 polymer was present on the external surface of the filaments for an L/D ratio of less than 3. At an L/D ratio of 3 or higher, the surface of the filaments was substantially devoid of nylon 6.

#### Example 7

Blend spinning was performed according to Example 3, but the yarn had a delta cross-section rather than a trilobal cross-section. A polypropylene-based master batch was used to produce a solution dyed yarn. Both beige and black color concentrates were used. The blend mixture had following composition: 72 wt.% polypropylene (PP), 20 wt.% nylon 6 (PA6), 6 wt.% maleic anhydride grafted polypropylene (PP-AM), 2 wt% color concentrate. The BCF yarn was extruded through a spinneret with delta cross-section holes. The shear rate inside the spinneret was 2900 reciprocal seconds and the L/D ratio of the spinneret was 3. The spin-drawn speed was 2500 m/min. Hot air texturizing was performed at 130°C. The drawing ratio was 4.5. After spinning, the resulting yarn had a yarn count of 650 dtex with 30 filaments. The yarn had a tenacity of 3.35 g/dtex (3.7 g/den), with an elongation at break of 45% and an increase in tenacity of 15% with respect of the 100 wt. % PP.

The yarn was dyed using an Ahiba machine using a disperse dye at 95°C for 30 minutes. The color fastness after washing was then determined. Washing was performed for 30 minutes using a water solution with a commercial shampoo at a pH of 7. The temperature at which color started to change was

recorded. Results indicated that only slight color changes occurred when washing at temperatures up to 85°C.

#### Example 8

Blend spinning was performed following the specification of Example 7 to produce a solution dyed yarn. Both beige and black color concentrates were used. The blend mixture had following composition: 72 wt% PP, 20 wt.% PA6, 6 wt.% PP-AM, 2wt% color concentrate. The BCF yarn was extruded through a spinneret with delta cross-section holes. The shear rate inside the spinneret was 2900 reciprocal seconds and the L/D ratio of the spinneret was 3. The spin-drawn speed was 2500 m/min. Hot air texturizing was performed at 130°C. The drawing ratio was 4.5. After spinning the resulting yarn had a yarn count of 650 dtex with 30 filaments.

The yarn had a tenacity of 3.05 g/dtex (3.4 g/den), with an elongation at break of 45% and an increase in tenacity of 15% with respect of the 100 wt. % PP.

The yarn was woven for use as upholstery, floor coverings, seating, trims, panels. Several cloth densities were manufactured as a function of the final application.

A wear resistance characterization was performed on the cloth with density of 11.6 yarns/cm, with a total density of 454 g/m<sup>2</sup>; the warp content was 46.6%, with a remaining weft density of 53.3%. The abrasion resistance of the cloth was tested using a nylon brush, with a force of 0.8 kg/cm<sup>2</sup> and compared to the resistance of a standard polyester based cloth manufactured using the same density after the same type of test. Testing of the polyester cloth was stopped after 2,500 cycles, and after 10,000 cycles for the claimed yarn. Results are presented in Figs.9a (polyester cloth after 2,500 brush cycles) and Fig.9b (cloth made with fiber according to Example 8 after 10,000 brush cycles).

### Examples 9

The claimed synthetic yarn was manufactured on a POY spinning plant. An 83 wt. % PP, 15 wt. % PA6, 2 wt. %PP-AM mixture was pre-blended and fed into the extruder after drying below 300 ppm of moisture. Spinning was performed at three speeds (2000, 2500 and 3000 m/min). A 100/24 POY yarn was produced. The resulting mechanical properties of the POY are presented in the following Table. After spinning an FDY was manufactured. A drawing ratio of 1.374 was applied, using a godet temperature of 60°C. Results are presented in Table 6.

Table 6

POY spinning speed	2000 m/min	2500 m/min	3000 m/min
POY dtex	99.9	99.6	99.1
POY Tenacity – cN/dtex	1.22	1.33	1.49
POY Elongation at break - %	279.31	249.46	214.77
Drawing ratio 1.374			
FDY dtex	75.5	77.1	78.3
FDY tenacity – cN/dtex	1.66	1.67	1.85
FDY Elongation at break - %	186.2	168.9	152.9
Drawing ratio 1.741			
FDY dtex	56	57.1	57.9
FDY tenacity – cN/dtex	2.23	2.43	2.75
FDY Elongation at break - %	74.3	68.7	64.3

The performance of the claimed synthetic yarn in terms of resilience and mechanical properties as a function of temperature was characterized at high temperatures and compared with the performances of the same yarn manufactured

using 100 wt.% PP. The effect of the heat treatment was also tested. The resilience of the yarn was evaluated using laboratory tests by imposing a deformation to the yarn and evaluating its capability to recover it after deloading. Tests were performed at room temperature and at higher temperatures. In the  
5 tests performed using the dynamic apparatus at the University of Trento, Department of Materials, a maximum deformation of 16 mm was imposed to the yarn with a frequency of 5 Hz. To test the yarn a static load of 0.05 N/dtex was applied onto a single filament. The effect of the temperature was achieved by increasing the temperature during the test at a rate of 3°C/min. Results are  
10 presented in Fig.10 for the FDY yarn manufactured at 3000 m/min. Curve (A) shows the behavior of yarn according to the invention made with 83 wt.% PP, 15 wt.%PA, while curve (B) shows the behavior of the same yarn after a heat treatment at 130°C for 5 minutes. For comparison, curve (C) indicated the deformation of the pure PP yarn without heat treatment and with the same heat  
15 treatment at 125°C for 5 min (Curve D).

Fig.10 demonstrated that the yarn made according to the invention (Curve A) provided a much higher shape retention at room temperature, when compared to 100 wt.% PP yarn (Curve C), which started to have a irreversible deformation above -20°C, i.e. above its glass transition temperature. At 25°C the  
20 deformation of the claimed yarn was below 3 %, indicating an excellent resilience, while the 100 wt.% PP yarn had already reached 30% of permanent deformation.

The tests also demonstrated much better mechanical properties of the yarn made according to the invention even at high temperature. In fact the permanent deformation of the yarn made according to the invention at 50°C is  
25 about only 10%, and only 20% (Curve B) if a thermal treatment at 130°C for 5 min was done. On the contrary more than 60% permanent deformation was observed for the pure PP yarn (Curve C), which exceed 100% if the yarn had been subjected to thermal treatment (Curve D).

Examples of use of yarn made according to the invention include but are not limited to: underwear, outerwear, sportswear, leisure, socks, apparel, strings, filters for the chemical industry.

5 Having described and illustrated preferred embodiments of the invention, it will be appreciated that various modifications, rearrangements and substitutions made to the invention by those of ordinary skill are within the spirit and scope of the appended claims.